PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C09J 7/02	A1	(11) International Publication Number: WO 99/35201 (43) International Publication Date: 15 July 1999 (15.07.99)

(21) International Application Number: PCT/US98/27875

(22) International Filing Date: 21 December 1998 (21.12.98)

(30) Priority Data:
10/403 5 January 1998 (05.01.98) JP

(71) Applicant *(for all designated States except US)*: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: ABE, Hidetoshi [JP/JP]; 11-32, Ekinishi 1-chome, Tendo-City, Yamagata Pref. 994-0047 (JP).

(74) Agents: HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: ADHESIVE SHEET AND METHOD FOR PRODUCING THE SAME

(57) Abstract

The problem in the art is to provide an adhesive sheet which can maintain a specific uneven structure just after the adhesion to an adherent so that bubbles can effectively escape even when the bubbles are trapped, and thereafter, the uneven structure deforms so that the deterioration of the appearance can be prevented after the adhesion. To solve that problem, an adhesive sheet comprising a flexible substrate film; an adhesive layer which is in contact with a main surface of the substrate sheet, and which has an uneven structure comprising projections which will be in contact with an adherent and grooves which are formed between adjacent projections and will communicate outside when the projections are in contact with the adherent; and a liner which has a negative structure corresponding to the uneven structure of the adhesive layer, and is laminated on the adhesive layer so that the negative structure and the uneven structure on the surface of the adhesive layer are in contact with each other, in which the adhesive layer comprises a crosslinked polymer, and maintains the uneven structure just after the adhesive sheet is adhered to the adherent, and the uneven structure deforms and a contact area increases to at least 92 %, or the adhesive layer comprises a matrix component containing an adhesive polymer and elastic microspheres which are dispersed in said matrix component and have a volume average diameter of 10 to 100 μm.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

ADHESIVE SHEET AND METHOD FOR PRODUCING THE SAME

Field of the Invention

The present invention relates to an improvement of an adhesive sheet which has a specific uneven structure on its adhesive surface, and can be adhered to an adherent without trapping unnecessary air between the adhesive surface and the surface of the adherent.

Background of the Invention

Adhesive sheets are known, which can be bonded or adhered to adherents without trapping unnecessary air between the adhesive surface and the surface of the adherent.

An example of such an adhesive sheet (including an adhesive film) comprises a substrate film and an adhesive layer which is in contact with at least one of the main surfaces of the substrate film, and which has an regularly patterned uneven structure comprising (i) a plurality of projections which will be in contact with an adherent and (ii) grooves which are formed between adjacent projections and will communicate outside when the projections are in contact with the adherent.

This type of the adhesive sheet can allow the trapped air bubbles to escape outside when it is in contact with an adherent and air bubbles are trapped between the adhesive surface of the sheet and the surface of the adherent. Thus, the adhesive sheet can be successfully adhered to the adherent without trapping the air between the adhesive surface of the sheet and the surface of the adherent.

Such adhesive sheets comprising adhesive layers having such an uneven structure described above are disclosed in, for example, Japanese Patent Publication JP-U (utility model)-3-67043-A.

A conventional method for producing an adhesive sheet will be briefly explained.

Firstly, a liner, an adhesive layer and a substrate film are laminated in this order to provide a laminate comprising these three layers.

Next, an embossing tool is pressed on the liner side of the laminate, and the laminate is processed so that a specific uneven structure is formed on the adhesive layer (adhesive surface). Therefore, the liner is made of a material which can be plastically deformed by above embossing, such as a resin film.

The substrate film of the usual adhesive sheet is also plastically deformed by above embossing, since it comprises a resin film. Thus, embossing marks remain on the main surface of the substrate film on which no adhesive layer is formed, and the appearance of the adhesive sheet deteriorates.

It is also known that a negative structure corresponding to a structure which will be formed on the surface of an adhesive surface is formed on the surface of a liner, a liquid containing an adhesive polymer is applied on the structural surface of the liner and solidified to form a laminate consisting of the liner and solidified adhesive layer, and then a resin substrate film is laminated on the surface of the adhesive layer to form an adhesive sheet (see, for example, U.S. Pat. No. 5,650,215 (Mazurek et al.)). In this method, the liner and adhesive layer are laminated so that the positive structure on the adhesive surface and the negative structure of the liner are in contact with each other. In this case, no embossing marks remain on the main surface.

However, none of the above prior art teach that the adhesive layers of the adhesive sheets having the uneven structure contain elastic microspheres.

Summary of the Invention

As described above, the adhesive sheets are known, which have no embossing marks on the main surface of the substrate film which is not in contact with the adhesive layer, and which can effectively prevent the deterioration of appearance.

However, with such an adhesive sheet, the uneven structure of the adhesive layer (i.e., adhesive surface) remains after the adhesion of the adhesive sheet to the adherent, and thus the shape of the uneven structure appears on the surface of the substrate film. Therefore, it is difficult to prevent the deterioration of the appearance of the adhesive sheet after the adhesion to the adherent. In particular,

with the flexible substrate film, depressions are formed in areas of the substrate film corresponding to the depressed portions of the adhesive layer, when the adhesive sheet are adhered to the adherent, and such depressed portions remain for a relatively long time after the completion of the adhesion.

Thus, an aspect of the present invention provides an adhesive sheet which can maintain a specific uneven structure just after the adhesion to an adherent so that bubbles can effectively escape even when the bubbles are trapped, and thereafter, the uneven structure deforms so that the deterioration of the appearance can be prevented after the adhesion.

The present invention provides an adhesive sheet comprising

(a) a flexible substrate film;

(b) an adhesive layer which is in contact with at least one of main surfaces of said flexible substrate sheet, and which has an uneven structure comprising (i) a plurality of projections which will be in contact with an adherent and (ii) grooves which are formed between adjacent projections and will communicate outside when said projection are in contact with the adherent; and

(c) a liner which has, on at least one of its surfaces, a negative structure corresponding to said uneven structure of the adhesive layer, and is laminated on said adhesive layer so that said negative structure and said uneven structure on the surface of the adhesive layer are in contact with each other.

Preferably, in one embodiment, the adhesive layer comprises a crosslinked polymer, and maintains said uneven structure just after the adhesive sheet is adhered to the adherent, and said uneven structure deforms and a contact area increases to at least 92 % after 48 hours at 25°C from the adhesion of the sheet to the adherent, or in the second embodiment, said adhesive layer comprises a matrix component containing an adhesive polymer and elastic microspheres which are dispersed in said matrix component and have a volume average diameter of 10 to 100 μm.

Further embodiments are disclosed below.

Embodiments of the Invention

Adhesive Sheet of One Embodiment

The adhesive sheet of the first embodiment according to the present invention has the following characteristics:

(a) the adhesive layer contains the crosslinked polymer, and

(b) the adhesive sheet maintains the uneven structure just after the liner is peeled off and the adhesive sheet is adhered to the adherent, and the uneven structure deforms and thus a contact area increases to at least 92 % after 48 hours at 25°C from the adhesion of the sheet to the adherent.

The above characteristic (b) is easily achieved by the use of the shape memory of the adhesive layer containing the crosslinked polymer. That is, such a characteristic is obtained by allowing the adhesive layer to memorize a flat shape having no uneven structure as the first shape, and then shaping the adhesive sheet to impart the specific uneven structure as the second shape to the adhesive layer. The easy and effective method for forming such an adhesive sheet will be explained below. In this case, the above liner, that is, the liner which has, on at least one of its surfaces, the negative structure corresponding to the uneven structure of the adhesive layer, and is laminated on the adhesive layer so that the negative structure and the uneven structure on the surface of the adhesive layer are in contact with each other, functions as a negative mold for imparting the above second shape (positive shape), and also as a protective film for maintaining the second shape of the adhesive layer during the storage (before use).

The adhesive layer contains an adhesive polymer, and has tackiness at room temperature (about 25°C). The crosslinked polymer may be the above adhesive polymer which has been crosslinked, or a separately added non-adhesive crosslinked polymer.

The polymer is usually crosslinked with a crosslinking agent. The amounts of the components are suitably selected in a range in which the adhesion force of the adhesive layer is not lower than a specified level, and the uneven structure deforms within a specific period of time and the contact area increases to 92 % or larger. For example, the adhesive layer may be formed from a liquid (coating

composition) for the adhesive layer containing 0.01 to 5 wt. parts of the crosslinking agent per 100 parts of the adhesive polymer contained in the adhesive layer.

To accelerate the crosslinking of the polymer, an energy such as heat and radiation can be preferably used. The polymer can be crosslinked by directly reacting reactive sites of the polymer chains.

Adhesive Sheet of Another Embodiment

In the adhesive sheet of the second embodiment, the adhesive layer comprises (1) the matrix component containing the adhesive polymer and (2) elastic microspheres dispersed in the matrix component and having a volume average diameter of 10 to 100 μm.

The elastic microspheres assist the recovery of the original shape of the adhesive layer after the adhesive layer is deformed from the originally imparted shape. For example, when the adhesive sheet is produced by forming the adhesive layer on the structural surface of the liner by the application and drying of the liquid for the adhesive layer, and then laminating the substrate film, the adhesive layer is formed, which has the uneven structure corresponding to the structural surface of the liner on the adhesive surface and a flat surface which is in contact with the substrate film. When such an adhesive sheet is adhered to an adherent and then pressed from the substrate film side against the adherent, the adhesive layer deforms, and depressed portions are formed on the surface of the substrate film at areas corresponding to the depressed portions of the adhesive layer (adhesive surface). However, the deformation of the adhesive layer is accompanied with the elastic deformation of the elastic microspheres, and thus, the adhesive layer recovers the original shape because of the shape recovering function of the elastic microspheres.

Such a shape recovery effect can be expected when the adhesive sheet is produced by the following method.

(1) the layer of an adhesive agent having a substantially flat adhesive surface is formed on at least one surface of the main surface of a substrate film,

which adhesive agent comprises a matrix component containing an adhesive polymer, and elastic microspheres dispersed in the matrix component, and

(2) then, the adhesive surface of the adhesive agent layer and the structural surface of a liner corresponding to the negative shape are allowed in contact with each other to form an adhesive layer having an uneven structure corresponding to the positive structure following the negative structure of the liner.

This method can produce the adhesive sheet which effectively and easily prevents the deterioration of the appearance of the adhesive sheet after the adhesion.

Source of Uneven Structure

The uneven structure of the adhesive layer is not limited, insofar as the effects of the present invention are not impaired.

The uneven structure comprises protrusions each having a horizontal section (a cross section in parallel with the adhesive surface) of a polygonal (e.g. square), round or similar shape, and grooves which are continuously formed to surround the projections.

The shape of a vertical section of each projection may be square such as trapezoidal or rectangular, semicircular or the like.

The height of the protrusion (the depth of the groove) is usually between 5 and 200 μm, preferably between 10 and 100 μm. When the protrusions are too low, it may be difficult to remove the bubbles trapped between the adhesive surface and adherent surface. When the protrusions are too high, the appearance of the adhesive sheet may be impaired after the completion of the adhesion.

The maximum width of the protrusion (the maximum size in the horizontal direction) is usually between 0.1 and 10 mm. The maximum width of the groove (the maximum distance between the adjacent protrusions) is usually between 0.05 and 1 mm.

The projections are preferably arranged regularly. For example, each projection is placed substantially at the center of each square of a check pattern. In this case, the grooves are formed along the lines constituting the check pattern, and

have one or more openings so that at least one groove, preferably a plurality of grooves can communicate with the outside.

The sizes of a plurality of projections and grooves are preferably all the same.

Elastic Microspheres

Herein, the "elastic microsphere", which may be referred to as "microsphere" simply, is intended to mean a material which exhibits rubbery elasticity as a whole.

The volume average diameter of the microspheres is usually between 10 and 100 μm, preferably between 20 and 80 μm. When the volume average diameter is less than 10 μm, the above shape recovery effect is not attained. When the volume average diameter exceeds 100 μm, the unevenness due to the presence of the microspheres may be recognized from the surface of the substrate film.

The volume average diameter is derived by measuring diameters of 1000 microspheres using an image analyzer with an optical microscope and calculating an average value according to the following equation (1):

$$\text{Volume average diameter } (\mu m) = \Sigma(d_i^4 \times n_i)/\Sigma(d_i^3 \times n_i) \qquad (1)$$

wherein d_i is a diameter (μm) of a microsphere having an i-th largest diameter, and n_i is the number of microspheres having the diameter d_i.

The microsphere may be a solid one or a hollow one having at least one void therein.

As a material of the microspheres, polyacrylate (acrylic copolymer) is preferred, since its rubbery elasticity and tackiness are easily controlled.

The compressive modulus of the microspheres is preferably in the range between 1×10^4 and 1×10^6 dyne/cm^2. In this range, the shape recovery effect of the microspheres is good.

The compressive modulus is measured using a RSA II viscoelastic spectrometer (manufactured by RHEOMETRIX) at 20°C. That is, the temperature

dependency of the modulus is measured by changing a temperature from -80°C to 150°C with applying a compression strain having a frequency of 1 rad/sec., and a measured value at 20°C is used as the compressive modulus.

The microspheres may be tacky or non-tacky. In general, the microspheres contain a crosslinked polymer.

Method for Producing Elastic Microspheres

The elastic microspheres may be produced by any known method such as suspension polymerization, emulsion polymerization, seed polymerization, and the like. A method for producing the microspheres of polyacrylate by emulsion polymerization will be briefly explained by way of example.

In a reactor equipped with a mechanical stirrer, deionized water, an acrylic monomer, a radical polymerization initiator, and other optional additives are added, and the interior of the reactor is purged with an inert gas. Then, the reactor is heated to a specific temperature to initiate polymerization of the monomer while stirring. In general, the stirring rate is from 10 to 700 rpm, and the reaction temperature is from 30 to 120°C. The reaction time is usually from several hours to several ten hours.

As the acrylic monomer, a mixture of an alkyl acrylate (e.g. isooctyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate, etc.) and an acrylic unsaturated acid (e.g. acrylic acid, methacrylic acid, itaconic acid, maleic acid, etc.) may be used. A weight ratio of the alkyl acrylate to the acrylic unsaturated acid is preferably from 99:1 to 90:10. When the amount of the alkyl acrylate is too small, the tackiness is lowered, while it is too large, the rubbery elasticity decreases. In either case, the adhesion force to the uneven surface tends to decrease. It is possible to crosslink the polyacrylate by the addition of a crosslinking agent comprising a bifunctional acrylate such as divinyl benzene 1,4-dibutyl-2-diacrylate to the above mixture.

The production method of the polyacrylate microspheres is disclosed in, for example, U.S. Patent No. 4,994,322.

The produced microspheres are usually recovered by filtration and used, while the as-produced aqueous dispersion containing the microspheres after the reaction can be used, and the tacky polymer is added to the dispersion to obtain the adhesive coating composition.

Adhesive Polymer

The "adhesive polymer" used herein means a polymer which exhibits adhesion at room temperature and can be used as a pressure sensitive adhesive. Polyacrylate, polyurethane, polyolefin, polyester, and the like can be used as such a polymer. A tackifier may be used in combination with the adhesive polymer, as in the case of conventional pressure sensitive adhesives. The adhesive polymer may be a polymer which can be cured with heat or radiation after the uneven structure of the adhesive layer deforms and the appearance of the adhesive sheet is improved insofar as the effects of the present invention are not impaired.

The molecular weight of the adhesive polymer may be in a range in which the desired viscosity is achieved. In general, the weight average molecular weight of the adhesive polymer is between 10,000 and 100,000.

The adhesive polymer can be used in the form of a solution (in which the polymer is dissolved in a solvent) or an emulsion (in which the polymer is dispersed in a solvent). The solution and emulsion may be used in admixture.

When the adhesive polymer is crosslinked, a crosslinking agent comprising an isocyanate compound, a melamine compound, a poly(meth)acrylate compound, an epoxy compound, an amide compound, and the like can be added. When the adhesive layer contains the non-adhesive polymer, the polymers can be crosslinked with such a crosslinking agent.

Adhesive Layer

In either the first or second embodiment, the thickness of the adhesive layer is not limited insofar as the effects of the present invention are not impaired, and is usually between 10 and 200 μm.

In the second embodiment, the amounts of the microspheres and adhesive polymer are selected so that the amount of the microspheres is usually between 5 and 500 wt. parts, preferably between 20 and 400 wt. parts, per 100 wt. parts of the adhesive polymer. When the amount of the microspheres is less than 5 wt. parts, the above shape recovery effect may not be attained. When such an amount exceeds 500 wt. parts, the adhesion force tends to decrease.

Substrate Film

As the substrate film, any one that is used as the substrate film of the conventional adhesive film may be used. For example, a paper sheet, a metal film, a plastic film and so on can be used. As the plastic, a synthetic polymer such as polyvinyl chloride, polyester, polyurethane, polyacrylate, polyolefin, etc. can be used. The thickness of the film is usually from 10 to 1500 μm.

The thickness of the film is usually between 10 and 500 μm. The surface of the substrate film on which the adhesive layer is formed may be treated to improve the adhesion force of the adhesive layer.

The contact area between the adhesive layer and adherent is defined as a ratio of a contacted area between the adhesive layer and the flat surface of a glass plate, when the adhesive sheet is adhered to the flat surface of the glass plate.

Concretely, the flat surface of a glass plate such as a slide glass and the adhesive layer of the adhesive sheet are adhered, and pressed by reciprocating a roller of 2 kg in weight over the film one time to obtain a sample. The width of the adhesive sheet is 2 cm so that a linear pressure is 1 kg/cm, and the roller is reciprocated in the longitudinal direction of the sheet.

When the glass plate is illuminated by a white light from the glass surface on which the adhesive film was not adhered, and the reflected light was observed through a polarized light filter, domains in which the projecting adhesive parts and the glass surface are in contact with each other are seen dark, while noncontact domains are seen white. The image is photographed, and a ratio of the total area of the contact domains to the area of the whole observed field (corresponding to the apparent contact area) is expressed in "percentage", which is used as the "contact

area rate". Such procedures can be carried out using an optical microscope equipped with a Polaroid camera. Here, the area of the whole observed field is usually about 1 cm^2. The surface roughness, Ra, of the used glass plate is 0.1 μm or less.

With the first embodiment, the observed contact area is usually 92 % or larger, preferably 95 % or larger, more preferably 98 % or larger, after the adhered sheet is maintained at 25°C for 48 hours and thus the uneven structure deforms.

Production of the Adhesive Sheet

The adhesive sheet of the first embodiment may be formed by applying a coating liquid for the adhesive layer on one or both of the surfaces of the substrate film, drying the applied coating liquid to form an adhesive layer, and pressing the uneven structural surface of a liner against the flat surface of the adhesive layer.

The coating liquid for the adhesive layer can be prepared by mixing the adhesive polymer, crosslinking agent, solvent and optional additives with a mixing apparatus such as a homomixer, a planetary mixer, etc. to disperse or dissolve all the components uniformly.

The prepared coating liquid is coated on the substrate film, and dried to form the adhesive layer. The coating liquid can be coated by any conventional coating means such as a knife coater, a roll coater, a die coater, a bar coater and the like. The coated liquid is usually dried at a temperature between 60 and 180°C. The drying time is usually between several ten seconds to several minutes.

Water or organic solvents can be used as solvents. Cosolvents which are partly miscible with water may be added. Examples of the useful co-solvents are alkyleneglycol monoalkyl ether esters such as 3-methyl-3-methoxybutyl acetate.

The coating liquid may contain conventional additives such as a viscosity modifier, an anti-foaming agent, a leveling agent, a UV light absorber, an antioxidant, a pigment, an anti-fungus agent, etc. In addition, the coating liquid may contain inorganic particles (e.g. glass beads, etc.) or organic particles other than the elastic microspheres, insofar as the effects of the present invention are not impaired.

The liner is usually made of a paper sheet, a plastic film, or a laminate film thereof. For example, an embossing tool having a positive shape is pressed onto the flat surface of the film, and the uneven structure corresponding to the negative shape is transferred to the film surface. During embossing, the tool can be heated. The above positive shape has the same shape and size as those of the uneven structure to be formed on the adhesive surface.

Alternatively, a flowable material comprising plastics is poured on a mold having a positive structure, and solidified. Then, the mold is removed, and the liner having the uneven structure corresponding to the negative shape is obtained.

The uneven structural surface of the liner may be treated with, for example, silicones to impart releasability. When the plastics are polyolefins, the releasing treatment may be omitted.

Alternatively, a marketed adhesive sheet is purchased, and the original liner is replaced with the above uneven liner. Then, the adhesive layer and uneven liner are pressed each other to impart the uneven structure to the adhesive layer.

The adhesive sheet of the second embodiment can be produced by applying the above coating liquid containing essentially the microspheres onto the uneven structural surface of the liner to form an adhesive layer, and then laminating a substrate film on the adhesive layer. The preparation of the coating liquid and coating method are the same as those for the first embodiment. The liner can be the same as that used in the first embodiment.

The adhesive surface having the uneven structure may be formed by pressing the uneven liner onto the adhesive layer having the substantially flat adhesive surface, which has been formed on the substrate film.

Use of the Adhesive Sheet

The adhesive sheet of the present invention can be used as a decorative sheet and adhered to walls, floors and ceilings of buildings, signboards, etc.

Further embodiments are described in the following Examples.

Examples

Example 1

The adhesive sheet of this Example is that of the first embodiment.

A. Adhesive sheet

SCOTCHCAL® JS1000A of Minnesota Mining and Manufacturing Company (3M) distributed by Sumitomo 3M Co. Ltd. of Tokyo, Japan, with a flat adhesive surface was used as the adhesive sheet, and the flat liner was replaced with a liner having an uneven surface which will be explained below, to form the uneven structure on the adhesive layer.

The adhesive layer of the above adhesive sheet was a layer formed by applying a coating composition comprising a crosslinked acrylic polymer and drying it, and had a thickness of 30 μm. The substrate film was a polyvinyl chloride film having a thickness of 50 μm.

B. Formation of Uneven Structure

On the adhesive surface of the adhesive sheet, a liner having an uneven structure was laminated while pressing to obtain an adhesive sheet having a liner.

The uneven structure of the liner consisted of a plurality of projections which were formed continuously along the lines which form a check pattern and corresponded to the grooves to be formed on the adhesive surface. The height of the projections was 17 μm, and the maximum distance (at the roots of the projections) between the adjacent projections was 1.2 mm. The depressed portion surrounded by the projections had the trapezoidal section in the vertical direction. Correspondingly, the protrusion on the adhesive layer had the trapezoidal cross section in the vertical direction.

C. Change of the Contact Area

On a flat surface of a slide glass of 76 mm in length, 26 mm in width and 1 mm in thickness (MICRO SLIDE GLASS HAKUROKUMA No. 1 manufactured by MATSUNAMI GLASS INDUSTRIES, Co., Ltd. of Japan), the adhesive layer of the adhesive sheet of about 5 cm x about 2 cm, from which the liner had been removed, was adhered and pressed by reciprocating a roller of 2 kg in weight and

about 4.5 cm in width over the film one time to obtain a sample. Then, the contact area of this sample was measured by the above method. The surface roughness, Ra, of the slide glass was about 0.001 μm.

The contact area of the adhesive sheet of this Example was 73 % just after the adhesion, and 100 % after maintaining the adhesive sheet at 25°C for 48 hours from the adhesion. After 48 hours at 25°C, the depressions of the substrate film corresponding to the depressions of the adhesive layer disappeared.

Bubble Escapability Test

After peeling off the liner, the adhesive sheet of 10 cm x 10 cm was placed on a flat acrylate plate, and squeezed by a squeezer towards the center of the adhesive sheet to gather bubbles. A roller of 2 kg was rolled over the bubbles several times, and a degree of the bubble escape was observed. When all the bubbles escaped, the film was ranked "GOOD", while when a part of bubbles remained, the film was ranked "NO GOOD".

The adhesive sheet of this Example was ranked "GOOD".

Comparative Example 1

An adhesive sheet was produced in the same manner as in Example 1 except that the coating liquid containing the same adhesive agent as that contained in the adhesive layer of the marketed adhesive sheet used in Example 1 was coated on the uneven structural surface of the liner and drying the coated liquid, and then laminating a polyvinyl chloride film.

The bubble escapability was "GOOD", but the depressions on the substrate film corresponding to the depressions of the adhesive layer did not disappear after 48 hours at 25°C. The contact area of the adhesive sheet of this Comparative Example was 81 % just after the adhesion, and 91 % after maintaining the adhesive sheet at 25°C for 48 hours from the adhesion.

Example 2

An adhesive sheet of this Example was produced in the same manner as in Example 1 except that another marketed adhesive sheet having a flat adhesive surface "CONTROL TACK PLUS® 180-10 of 3M was used as an adhesive sheet.

The adhesive layer of this adhesive sheet contained a crosslinked acrylic polymer and glass microbeads, and had a thickness of 30 μm. The substrate film was the polyvinyl chloride film like the above used adhesive sheet.

The bubble escapability was "GOOD", and the depressions on the substrate film corresponding to the depressions of the adhesive layer disappeared after 48 hours at 25°C. The contact area of the adhesive sheet of this Comparative Example was 91 % just after the adhesion, and 100 % after maintaining the adhesive sheet at 25°C for 48 hours from the adhesion.

Example 3

The adhesive sheet of this Example is that of the second embodiment.

An aqueous emulsion type adhesive "E-1000" (manufactured by SOKEN CHEMICAL Co., Ltd. of Japan) was used as a liquid containing a matrix component comprising an adhesive polymer. The adhesive polymer consisted of butyl acrylate and acrylic acid in a weight ratio of 96:4.

The elastic microspheres were prepared by the suspension polymerization using water as a medium according to the above described method. The used monomer composition contained isooctyl acrylate and acrylic acid in a weight ratio of 96:4. The compression modulus was 7×10^5 dyn/cm^2. The compression modulus was measured as follows:

The solvent was removed from the suspension containing the elastic microspheres, and the microspheres were shaped in a cylinder form having a diameter of 5 mm and a length of 7 mm to obtain a test sample. The sample was attached to parallel plate jigs and then a compression modulus was measured under the above measuring conditions.

The above elastic microspheres were added to the emulsion containing the above adhesive polymer in such amounts that a weight ratio of the adhesive

polymer to the elastic microsphere was 80:20 (solid weights), and mixed to obtain a substantially uniform coating dispersion. The coating dispersion was applied on the uneven surface of the liner and dried to solidify it. On the dried layer, the above polyvinyl chloride substrate film having a thickness of 70 μm was laminated. Thus, an adhesive sheet consisting of the liner, adhesive layer and substrate film which were laminated in this order was obtained. The thickness of the adhesive layer was 30 μm.

The bubble escapability was "GOOD", and the depressions on the substrate film corresponding to the depressions of the adhesive layer disappeared after 48 hours at 25°C.

For an appreciation of the scope of the invention, the claims follow.

What is claimed is:

1. An adhesive sheet comprising a flexible substrate film;

an adhesive layer which is in contact with at least one of main surfaces of said flexible substrate sheet, and which has an uneven structure comprising (i) a plurality of projections which will be in contact with an adherent and (ii) grooves which are formed between adjacent projections and will communicate outside when said projections are in contact with the adherent; and

a liner which has, on at least one of its surfaces, a negative structure corresponding to said uneven structure of the adhesive layer, and is laminated on said adhesive layer so that said negative structure and said uneven structure on the surface of the adhesive layer are in contact with each other, wherein said adhesive layer comprises a crosslinked polymer, and maintains said uneven structure just after the adhesive sheet is adhered to the adherent, and said uneven structure deforms and a contact area increases to at least 92 % after 48 hours at 25°C from the adhesion of the sheet to the adherent.

2. An adhesive sheet comprising a flexible substrate film;

an adhesive layer which is in contact with at least one of main surfaces of said flexible substrate sheet, and which has an uneven structure comprising (i) a plurality of projections which will be in

contact with an adherent and (ii) grooves which are formed between adjacent projections and will communicate outside when said projections are in contact with the adherent; and

a liner which has, on at least one of its surfaces, a negative structure corresponding to said uneven structure of the adhesive layer, and is laminated on said adhesive so that said negative structure and said uneven structure on -the surface of the adhesive layer are in contact with each other, wherein said adhesive layer comprises a matrix component containing an adhesive polymer and elastic microspheres which are dispersed in said matrix component and have a volume average diameter of 10 to 100 μm.

3. A method for producing an adhesive sheet claimed in claim 1, comprising the steps of:

(1) applying, on said main surface of said substrate film, a composition which comprises 100 wt. parts of an adhesive polymer and 0.01 to 5 wt. parts of a crosslinking agent, solidifying said composition to form a layer of an adhesive agent with a substantially flat surface, and then crosslinking said adhesive polymer; and

(2) allowing the surface of said liner having said negative structure in contact with said substantially flat surface of said adhesive agent layer to form the adhesive layer having said uneven structure which has a positive structure following said negative structure.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/27875

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 268 228 A (ORR ROBERT B) 7 December 1993	1
Y	see column 2, line 13 - line 31 see column 3, line 7 - line 29 see column 3, line 41 - line 46 see column 3, line 52 - line 58 see example 1 see claims 1,2,12-16	3
Y	EP 0 279 579 A (BRIDGESTONE CORP) 24 August 1988	3
A	see page 2, line 27 - line 34 see page 3, line 6 - line 15 see page 4, line 19 - line 34 see figures 1-3	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 April 1999	14/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schlicke, B

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/27875

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 20008 A (MINNESOTA MINING & MFG) 5 June 1997 see abstract see page 5, line 23 - line 28 see page 6, line 25 - line 29 see page 9, line 8 - line 12 see figure 1 ---	2
P,X	WO 98 29516 A (MINNESOTA MINING & MFG) 9 July 1998 see page 10, line 12 - page 11, line 5 see examples 1-4,98-100 -----	1,3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/27875

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5268228 A	07-12-1993	NONE	
EP 0279579 A	24-08-1988	JP 63193982 A JP 63223081 A DE 3880341 A	11-08-1988 16-09-1988 27-05-1993
WO 9720008 A	05-06-1997	JP 9157606 A AU 1123697 A EP 0863956 A	17-06-1997 19-06-1997 16-09-1998
WO 9829516 A	09-07-1998	AU 3290897 A	31-07-1998